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Anodic oxidation effects on pyrolytic graphite surfaces in acid

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Anodic oxidation effects on the basal and edge surfaces of pyrolytic graphite in acid were studied by laser Raman spectroscopy, and by a gas-phase chemical modification method coupled with X-ray photoelectron spectroscopy. Surface covering fractions were also studied by α-epichlorohydrin monolayer formation. It was found that the species of surface chemical groups added by anodic oxidation was closely related to the structure of the oxidized surface. In the case of the basal surface, carboxyl groups were added by anodic oxidation, being always accompanied by the destruction of its surface structure. On the other hand, in the case of the edge surface, hydroxyl groups were added without the destruction of its structure with a mild treatment. With more severe treatment, carboxyl groups were added and this addition was also accompanied by destruction of the surface structure. There was a range of treatment in which hydroxyl groups could be added without destroying the structure. Finally it was confirmed that both carboxyl and hydroxyl groups could make covalent bonds with epoxy groups of α-epichlorohydrin.

1. Introduction

Oxidative surface treatment of carbon fibres (CFs) improves the shear strength of CF–epoxy matrix composites [1–4]. On the other hand, excessive surface treatment reduces both the longitudinal and shear strength of the composites [5]. In order to optimize the surface treatment of CFs, it is necessary to characterize the nature of CF surface before and after the treatment and to understand the interface between CFs and matrices. Drzal [6] concluded that surface treatments designed to promote adhesion to epoxy matrix materials operate through a two-part mechanism. First, the treatments remove a weak outer fibre layer initially present on the fibre. Second, the treatments add surface chemical groups which contribute to the interaction with the matrix materials. Kozlowski and Sherwood [7], using X-ray photoelectron spectroscopy (XPS), suggested that carboxylic/ester groups are added at the edge sites in the CF surface whereas keto–enol groups are added to the basal planes. Denison and Jones [8], using trichloromethane labelling and XPS, proposed that functional groups are bound to edge carbon atoms in the micropores of CFs. However, it is difficult to characterize the relationship between the structure of CF surfaces and the species of surface chemical groups added by surface treatments, since the structure of CFs is complicated and then do not show a homogeneous surface.

The nature and the relationship mentioned above were studied by using the basal and edge surfaces of pyrolytic graphite (PG) as a model CF surface. In this paper the effect of anodic oxidation on the basal and edge surfaces of PG in acid is discussed with respect to the chemical and physical properties of their surfaces and the interaction of surface chemical groups added to their surfaces with α-epichlorohydrin.

2. Experimental procedure

PG from Union Carbide Corporation was used in the present study. Mirror-polished edge surfaces of PG, which are parallel to the *c*-axes of graphite crystallites, were prepared by the method of Katagiri *et al.* [9]. Basal surfaces, which are perpendicular to the *c*-axes of graphite crystallites, were prepared by cleaving PG. These surfaces were ultrasonically rinsed three times in trichloroethylene, acetone and distilled water in that order, and then dried at 100 °C. The basal and edge surfaces were oxidized anodically in sulphuric acid solutions (0.1 N). The specific electric charge (electric charge (C) per unit area (m^2)) was controlled by changing the current density with a potentiometer (Hokutodenko HJ-2010), keeping the treatment time at 10 sec. Anodic oxidation was carried out in four steps: 50, 125, 500 and 5000 $C\,m^{-2}$ on the basal and edge surfaces. After the surface treatments, the surfaces were again rinsed in distilled water and dried at 100 °C.

Laser Raman spectroscopy was used to characterize the structural changes of the unoxidized and oxidized surfaces. Raman spectra of the surfaces were measured by using a double-grating monochromator (Jobin Yvon Ramanor U-1000) with a cooled photomultiplier tube (Hamamatsu R-1104).

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A gas-phase chemical modification (GCM) method coupled with XPS [10] was used for detecting hydroxyl and carboxyl groups on the basal and edge surfaces. Trifluoroacetic anhydride (TFAA) was used to label hydroxyl groups. Trifluoroethanol (TFE) and dicyclohexylcarbodiimide (DCCDI) were used to label carboxyl groups. A spectrometer (SSI SSX-100-206) with a monochromatized Al$K\alpha_{1,2}$ X-ray anode ($h\nu = 1486.6$ eV) was used for XPS measurement in a vacuum of 3×10^{-9} torr.

Chemical treatment of both unoxidized and oxidized surfaces with α-epichlorohydrin was carried out by refluxing the basal and edge surfaces in contact with α-epichlorohydrin for 10 h. After the chemical treatment, the surfaces were ultrasonically rinsed for 15 min in acetone and distilled water and dried for 30 min at 100 °C. The fraction (q) of the surface covered by an α-epichlorohydrin monolayer was estimated by using the method proposed by Waltersson [11].

3. Results and discussion

The Raman spectra of the unoxidized and oxidized basal surfaces of PG are shown in Fig. 1. Two Raman bands were observed at 1580 and 1355 cm^{-1}. These two Raman bands are ascribed to the in-plane motions of carbon atoms in the graphite basal planes. The former band is associated with a doubly degenerated stretching vibrational mode (E_{2g}) of the infinite graphite basal planes, whereas the latter is associated with a vibrational mode (A_{1g}) originating from disordered structure in the basal layer such as edges and lattice vacancies [12]. Therefore the intensity ratio (R) of the 1355 cm^{-1} band to the 1580 cm^{-1} band of PG can be related to the amount of edges and vacancies in the surfaces of PG [9]. A marked change in the spectra is recognized in the range 500 to 5000 C m^{-2}. The R of the basal surface oxidized at 5000 C m^{-2} is markedly larger than those of others. A shoulder around 1620 cm^{-1} is also recognized in the surface oxidized at 5000 C m^{-2} and is considered to be due to a hexagonal ring stretching mode which is slightly modified by the formation of carbon–oxygen complexes [13]. Consequently, the increase in R for wavenumber 1355 cm^{-1} and the shoulder around 1620 cm^{-1} can be considered as evidence that the structure of the basal surface is destroyed and many carbon–oxygen complexes are added at the surface.

Fig. 2 shows the Raman spectra of the unoxidized and oxidized edge surfaces, measured with the incident laser radiation polarized parallel to the edge surface. The spectra measured with a perpendicular configuration are much the same as those measured with a parallel one. Also, a marked change of the spectrum is recognized at the edge surface in the range 500 to 5000 C m^{-2}. Thus the structure of the edge surface is considered to be destroyed at 5000 C m^{-2}. The value of R of the unoxidized edge surface is higher than that of the unoxidized basal one. Distinct bands appear around 1620 cm^{-1} in the unoxidized and oxidized edge surfaces. These spectral features seem not to be due to the disorder of basal planes near the edge surfaces caused by polishing, but to the discontinuity of basal planes at the edge surfaces [9].

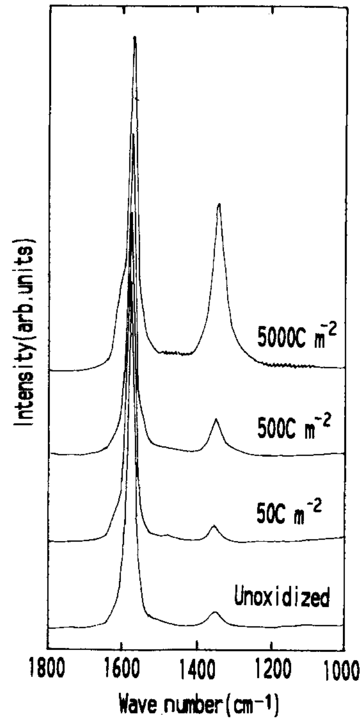

Figure 1 Raman spectra of the unoxidized and oxidized basal surfaces of PG.

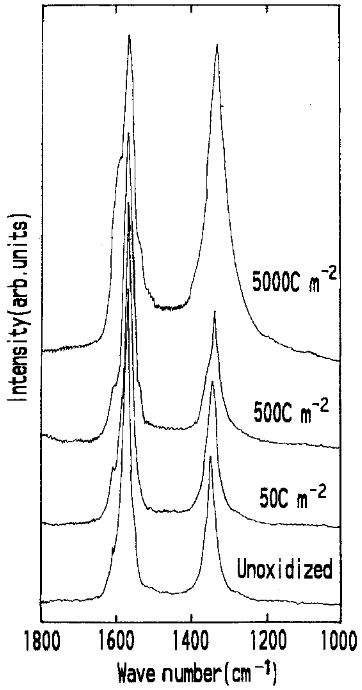

Figure 2 Raman spectra of the unoxidized and oxidized edge surfaces of PG measured with incident laser radiation polarized parallel to the edge surface.

XPS wide-scan spectra (Fig. 3) show the basal and edge surfaces of PG after the reaction with TFE and DCCDI. The spectra of the unoxidized basal and edge surfaces have weak Fls peaks, whereas the spectra of the basal and edge surfaces oxidized at 5000 C m^{-2} have more intense Fls peaks at 689 eV. This confirms the successful labelling of carboxyl groups at the basal and edge surfaces.

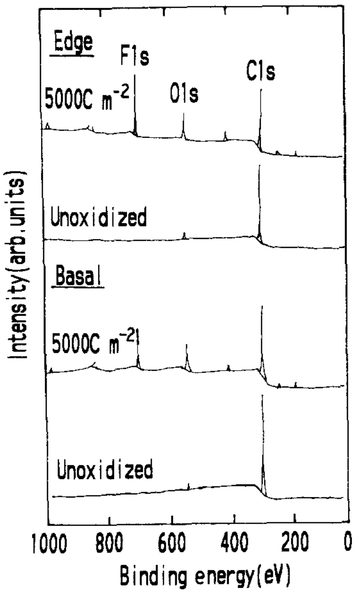

Figure 3 XPS wide-scan spectra of the basal and edge surfaces of PG treated with TFE and DCCDI.

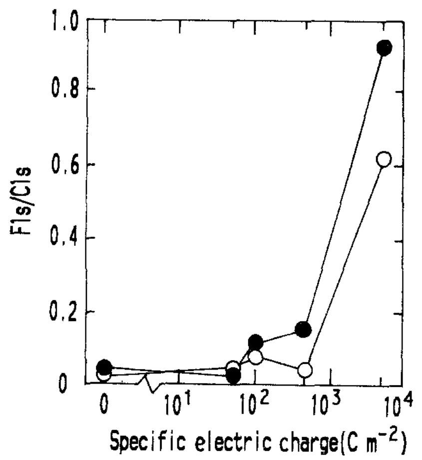

Figure 4 Change of the relative fluorine concentration (Fls/Cls) with specific electric charge for (○) basal and (●) edge surfaces of PG treated with TFE and DCCDI.

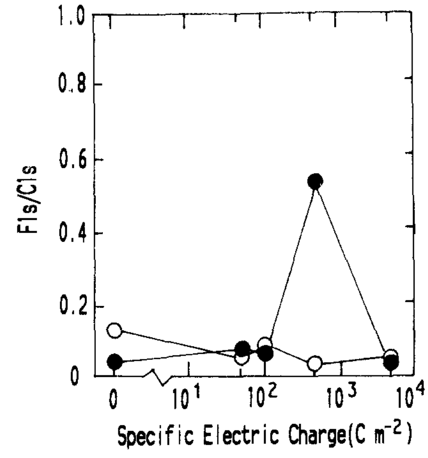

Figure 5 Relation between the relative fluorine concentration (Fls/Cls) and specific electric charge for (○) basal and (●) edge surfaces of PG treated with TFAA.

Fig. 4 shows the change of relative fluorine concentration (Fls/Cls) with specific electric charge for the basal and edge surfaces of PG treated with TFE and DCCDI. The increase of the Fls/Cls ratio means an increase of the amount of carboxyl groups. In the case of the edge surface, the amount of carboxyl groups increases with increasing specific electric charge. The increase is especially large when the specific electric charge increases from 500 to 5000 C m^{-2}. In the basal surface, a marked increase of the amount of carboxyl groups is not found up to 500 C m^{-2}. In the range of specific electric charge from 500 to 5000 C m^{-2}, the amount of carboxyl groups increases rapidly.

As stated above, the Raman spectral results indicate that the basal and edge surface structures are destroyed at 5000 C m^{-2}. The rapid increase in the amount of carboxyl groups at the basal and edge surfaces in the range 500 to 5000 C m^{-2}, is considered to be related to the destruction of their surface structure. A large quantity of carboxyl groups is expected to be added at the discontinuity of broken basal and edge surface structures.

Fig. 5 shows the relation between the Fls/Cls ratio and the specific electric charge for the basal and edge surfaces of PG treated with TFAA. The increase of this ratio means an increase of the amount of hydroxyl groups. When the specific electric charge increases from 125 to 500 C m^{-2}, a rapid increase of the amount of hydroxyl groups is recognized only on the edge surface. On the other hand, the amount of hydroxyl groups does not show a rapid increase in the range 500 to 5000 C m^{-2}.

Therefore, in the anodic oxidation of the edge surface in the sulphuric acid electrolyte, it is possible to add a large quantity of hydroxyl groups on the edge surface without destroying its structure. From the results described above, it is seen that the surface structure and the species of surface chemical groups added by the anodic oxidation have a close relationship. That is to say, when the edge surface is oxidized anodically without destruction of the structure, hydroxyl groups are added on the edge surface. On the other hand, hydroxyl groups are not added on the basal surface by anodic oxidation. Carboxyl groups are added on the basal surface only when the basal planes at the surface are destroyed by anodic oxidation. So it is possible to estimate CF surface structure (the edge/basal plane ratio) from the –OH/–COOH ratio on the CF surface.

The XPS scan (Fig. 6) shows the spectra of the basal and edge surfaces treated with α-epichlorohydrin. The spectra of the unoxidized basal and edge surfaces have very weak Cl2p peaks, whereas the spectra of the basal and edge surfaces oxidized at 5000 C m^{-2} have more intense Cl2p peaks at 200 eV. This confirms that α-epichlorohydrin is covalently bonded to the basal and edge surfaces.

Fig. 7 shows the Cl2p/Cls ratio (q) of the basal and edge surfaces treated with α-epichlorohydrin plotted against the specific electric charge. In the range 125 to 500 C m^{-2}, where an increase of the amount of hydroxyl groups is recognized on the edge surface, the increase of q is large. In the range 500 to 5000 C m^{-2}, where an increase of the amount of carboxyl groups is recognized on both the basal and edge surfaces, the increase of q is also large. Therefore, these results

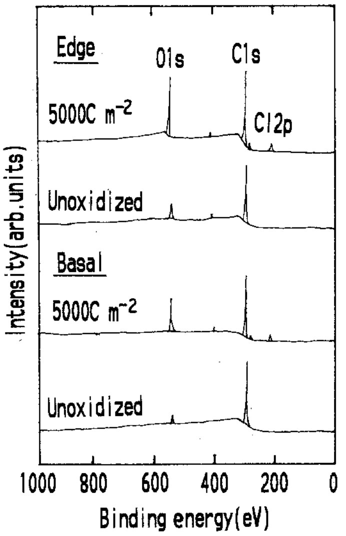

Figure 6 XPS wide-scan spectra of the basal and edge surfaces of PG treated with α-epichlorohydrin.

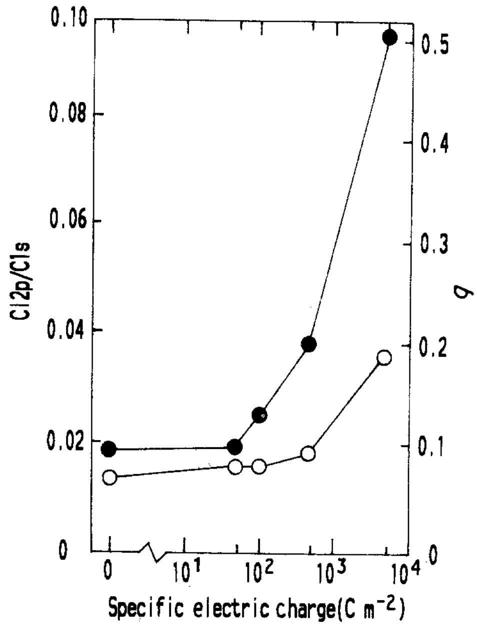

Figure 7 Relative chlorine concentration (Cl2p/Cls), or the fraction (*q*) of the surface covered by an α-epichlorohydrin monolayer, against the specific electric charge for (○) basal and (●) edge surfaces of PG treated with α-epichlorohydrin.

indicate that α-epichlorohydrin is covalently bonded through its epoxy group to hydroxyl or carboxyl groups on the basal or edge surface.

The edge surface, having many hydroxyl groups, is considered to be very important in improving the shear strength of CF–epoxy matrix composites. This is because hydroxyl groups at the edge surface form covalent bonds with both epoxy groups and internal carbon atoms bound by strong covalent forces to preserve the hexagonal array. On the other hand, the basal and edge surfaces, having many carboxyl groups, are not considered to be so important in improving the shear strength of the composite. The reason is as follows. In the case of the basal surface, carboxyl groups at the basal surface form strong covalent bonds with epoxy groups, but the atoms at the basal surface form weak Van der Waals bonds with internal basal planes. In the case of the edge surface, carboxyl groups at the edge surface also form strong covalent bonds with epoxy groups, but the bonding between carbon atoms bonded with carboxyl groups at the edge surface and internal ones becomes weaker through the partial destruction of sp^2 bonds between the carbon atoms.

4. Conclusions

By anodic oxidation, hydroxyl groups are added to the edge surface of PG without destroying its structure at 500 C m^{-2} and form covalent bonds with epoxy groups. Thus the edge surface is considered to have a very important role in improving the shear strength of CF–epoxy matrix composites. Carboxyl groups are initially added to the basal and edge surfaces in the range 500 to 5000 C m^{-2}, where the structure of the surface is destroyed, and also form covalent bonds with epoxy groups. In this case, the bonding between atoms located in the surfaces and internal ones will become weaker when the amount of carboxyl groups on the surfaces increases. Therefore, in the range of higher specific electric charge, the basal and edge surface structures, having many carboxyl groups, may reduce the shear strength of the composites.

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